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(54) Title: SELECTIVE HYDROGENATION OF HIGHLY UNSATURATED COMPOUNDS IN HYDROCARBON STREAMS (57) Abstract <p>A process for the selective hydrogenation of the diolefins and acetylenic compounds in an olefin-rich aliphatic hydrocarbon stream (1) comprises contacting the feed stream (1) at 40-300 °F under low hydrogen partial pressure of 0.1-70 psia at a total pressure of 0-350 psig in a distillation column reactor (10) containing a hydrogenation catalyst bed (12) which serves as a component of a distillation structure (10), such as supported PdO encased in a tubular wire mesh. Essentially no hydrogenation of the olefins occur. The feed stream (1) enters below or at the lower end of the catalyst bed (12), and is contacted with hydrogen fed through line (2) in the catalyst bed (12). The overhead (3) is obtained at the overhead, condensed in a condenser (20) and separated in a settler (30), and partially recycled back to catalyst bed (12) as a reflux stream (6). The bottom stream (11) is obtained at the lower end of the distillation reactor, and is partially recycled back as stream (4) after being heated in a heat exchanger (40) as recycle stream (13). Net hydrogenation effluent is obtained as stream (9), and light gases as stream (7).</p>		

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SELECTIVE HYDROGENATION OF HIGHLY
UNSATURATED COMPOUNDS IN HYDROCARBON STREAMS

This application is a continuation in part of USSN 07/933,753 filed 08/24/92 and USSN 08/079,975 filed 06/21/93 which was a continuation of USSN 07/833,360 filed 02/10/92 now abandoned.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the selective hydrogenation of diolefins and acetylenic compounds in a olefin rich stream. More particularly the invention relates to a process utilizing a hydrogenation catalyst in a structure to serve as both the catalyst and as a distillation structure for the simultaneous reaction and separation of the reactants and reaction products.

Related Art

Mixed refinery streams often contain a broad spectrum of olefinic compounds. This is especially true of products from either catalytic cracking or thermal cracking processes. These unsaturated compounds comprise ethylene, acetylene, propylene, propadiene, methyl acetylene, butenes, butadiene, amylenes, hexenes etc. Many of these compounds are valuable, especially as feed stocks for chemical products. Ethylene, especially is recovered. Additionally, propylene and the butenes are valuable. However, the olefins having more than one double bond and the acetylenic compounds (having a triple bond) have lesser uses and are detrimental to many of the chemical process in which the single double bond compounds are used, for example polymerization. Over the range of hydrocarbons under consideration, the removal of highly unsaturated compounds is of value as a feed pretreatment, since these compounds have frequently been found to be detrimental in most processing, storage and use of the streams.

The C₄ cuts are sources of alkanes and alkenes for paraffin alkylation to produce C₈ gasoline blending components and as feeds for ether production.

The C₅ refinery cut is valuable as a gasoline blending stock or as source of isoamylene to form an ether by reaction with lower alcohols. Tertiary amyl methyl ether (TAME) is rapidly becoming valuable to refiners as a result of the recently passed Clean Air Act which sets some new limits on gasoline composition. Some of these requirements are (1) to include a certain amount of "oxygenates", such as methyl tertiary butyl ether (MTBE), TAME or ethanol, (2) to reduce the amount of olefins in gasoline, and (3) to reduce the vapor pressure (volatility).

The C₅'s in the feed to a TAME unit are contained in a single "light naphtha" cut which contains everything from C₅'s through C₈'s and higher. This mixture can easily contain 150 to 200 components and thus identification and separation of the products is difficult. Several of the minor components (diolefins) in the feed will react slowly with oxygen during storage to produce "gum" and other undesirable materials. However, these components also react very rapidly in the TAME process to form a yellow, foul smelling gummy material. Thus it is seen to be desirable to remove these components whether the "light naphtha" cut is to be used only for gasoline blending by itself or as feed to a TAME process.

The use of a solid particulate catalyst as part of a distillation structure in a combination distillation column reactor for various reactions is described in U.S. Pat. No.s: (etherification) 4,232,177; 4,307,254; 4,336,407; 4,504,687; 4,918,243; and 4,978,807; (dimerization) 4,242,530; (hydration) 4,982,022; (dissociation) 4,447,668; and (aromatic alkylation) 4,950,834 and 5,019,669. Additionally U.S. Pat. No.s 4,302,356 and 4,443,559 disclose catalyst structures which are useful as distillation structures.

Hydrogenation is the reaction of hydrogen with a carbon-carbon multiple bond to "saturate" the compound. This reaction has long been known and is usually done at super atmospheric pressures and moderate temperatures using a large excess of hydrogen over a metal catalyst. Among the

metals known to catalyze the hydrogenation reaction are platinum, rhenium, cobalt, molybdenum, nickel, tungsten and palladium. Generally, commercial forms of catalyst use supported oxides of these metals. The oxide is reduced to the active form either prior to use with a reducing agent or during use by the hydrogen in the feed. These metals also catalyze other reactions, most notably dehydrogenation at elevated temperatures. Additionally they can promote the reaction of olefinic compounds with themselves or other olefins to produce dimers or oligomers as residence time is increased.

Selective hydrogenation of hydrocarbon compounds has been known for quite some time. Peterson, et al in "The Selective Hydrogenation of Pyrolysis Gasoline" presented to the Petroleum Division of the American Chemical Society in September of 1962, discusses the selective hydrogenation of C₄ and higher diolefins. Boitiaux, et al in "Newest Hydrogenation Catalyst", Hydrocarbon Processing, March 1985, presents a general, non enabling overview of various uses of hydrogenation catalysts, including selective hydrogenation of a propylene rich stream and other cuts. Conventional liquid phase hydrogenations as presently practiced required high hydrogen partial pressures, usually in excess of 200 psi and more frequently in a range of up to 400 psi or more. In a liquid phase hydrogenation the hydrogen partial pressure is essentially the system pressure.

U.S. Pat. No. 2,717,202 to Bailey discloses a countercurrent process for the hydrogenation of lard carried out in a plurality of independent vertical chamber using a pumped catalyst under undisclosed pressure conditions. U.S. Pat. No. 4,221,653 to Chervenak et al discloses a concurrent hydrogenation for using an ebullating bed at extremely high pressures. UK Patent Specification 835,689 discloses a high pressure, concurrent trickle bed hydrogenation of C₂ and C₃ fractions to remove acetylenes.

U.S. Pat No. 5,087,780 to Arganbright disclosed a

process for the hydroisomerization of butenes using an alumina supported palladium oxide catalyst arranged in a structure for use as both the catalyst and distillation in a catalytic distillation reactor. The hydrogenation of
5 dienes was also observed under high hydrogen partial pressure, in excess of 70 psia, but not at around 10 psia.

It is an advantage of the present process that the diolefins (dienes) and acetylenic compounds contained within the hydrocarbon stream contacted with the catalyst
10 are converted to olefins or alkanes with very little if any formation of oligomers or little if any saturation of the mono-olefins.

SUMMARY OF THE INVENTION

The present invention comprises feeding a hydrocarbon
15 stream containing highly unsaturated compounds which comprise diolefins and acetylenes along with a hydrogen stream at an effectuating hydrogen partial pressure of at least about 0.1 psia to less than 70 psia, preferably less than 50 psia to a distillation column reactor containing a
20 hydrogenation catalyst which is a component of a distillation structure and selectively hydrogenating a portion of the highly unsaturated compounds. Within the hydrogen partial pressures as defined no more hydrogen than necessary to maintain the catalyst (most likely to reduce
25 the catalyst metal oxide and maintain it in the hydride state) and hydrogenate the highly unsaturated compounds is employed, since the excess hydrogen is usually vented. This preferably is a hydrogen partial pressure in the range of about 0.1 to 10 psia and even more preferably no more
30 than 7 psia. Optimal results have been obtained in the range between 0.5 and 5 psig hydrogen partial pressure.

The hydrocarbon stream typically comprises C₂ to C₉ aliphatic compounds, which may be narrow cuts or include a range of carbon content. The invention is the discovery
35 that a hydrogenation carried out in a catalytic distillation column requires only a fraction of the hydrogen partial pressure required in the liquid phase processes which are the form of prior commercial operation

for this type of stream, but give the same or better result. Thus the capital investment and operating expense for the present hydrogenation are substantially lower than prior commercial operations.

5 Without limiting the scope of the invention it is proposed that the mechanism that produces the effectiveness of the present process is the condensation of a portion of the vapors in the reaction system, which occludes
10 sufficient hydrogen in the condensed liquid to obtain the requisite intimate contact between the hydrogen and the highly unsaturated compounds in the presence of the catalyst to result in their hydrogenation.

The highly unsaturated compounds may be present in very minor amounts, i.e., a few parts per million up to major
15 amounts, i.e., over 90 weight %. The present invention may be used to remove impurities or to convert commodity amounts of the highly unsaturated compounds into monoolefins or alkanes as desired.

The hydrogen rate must be adjusted at the partial
20 pressure described such that it is sufficient to support the hydrogenation reaction and replace hydrogen lost from the catalyst but kept below that producing hydrogenation of monoolefins which is understood to be the "effectuating hydrogen partial pressure" as that term is used herein.

25 As can be readily appreciated the amount of the highly unsaturated compound in the hydrocarbon stream is a factor to be considered in selecting the optimum hydrogen partial pressure, since at least a stoichiometric amount of hydrogen must be present in the system to be available for
30 the reaction. When the highly unsaturated compounds are impurities, present in parts per million the lower range of hydrogen partial pressure is a an excess, but it is necessary because of the scarcity of the selective reactant. Also the nature of this reaction between a gas
35 and a liquid and the apparent need to occlude the hydrogen into the liquid makes an excess of hydrogen within the partial pressures a preferred mode of operation.

An additional feature of the process is that a portion

of the mono-olefins contained within the stream or produced by the selective hydrogenation of the diolefins may be isomerized to more desirable products. Isomerization can be achieved with the same family of catalysts as used in hydrogenations. Generally the relative rates of reaction for various compounds are in the order of from faster to slower:

- (1) hydrogenation of diolefins
- (2) isomerization of the mono-olefins
- (3) hydrogenation of the mono-olefins.

It has been shown generally that in a stream containing diolefins, the diolefins will be hydrogenated before isomerization occurs. It has also been found that very low total pressures may be used for optimal results in some of the present hydrogenations, preferably in the range of 50 to 150 psig with the same excellent results. Both higher and lower pressures within the broad range may be used may be used with satisfactory results.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a simplified flow diagram of one embodiment of the present invention.

FIG. 2 is a simplified flow diagram of a second embodiment of the present invention.

FIG. 3 is a simplified flow diagram of a third embodiment of the present invention.

FIG. 4 is a simplified flow diagram of a fourth embodiment of the present invention.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

Although the hydrogenation reactions have been described as reversible at elevated temperatures above about 900°F (See for example the Peterson article cited above) under the temperature conditions employed in the present invention, the hydrogenation is not reversible. In the usual application of a process where the catalyst serves as a distillation component, the equilibrium is constantly disturbed, thus driving the reaction toward completion, that is, the reaction has an increased driving force because the reaction products have been removed and cannot

contribute to a reverse reaction (LeChatelier's Principle). In the present process where there is no reversible reaction, no benefit is to be derived by removing the products of the reaction to increase the driving force of the reaction by. Similarly the poor performance of prior vapor phase hydrogenations would not suggest the use of distillation type reaction. Thus, it is unexpected that catalytic distillation would be of benefit for non reversible hydrogenation.

It is believed that in the present reaction catalytic distillation is a benefit first, because the reaction is occurring concurrently with distillation, the initial reaction products and other stream components are removed from the reaction zone as quickly as possible reducing the likelihood of side reactions. Second, because all the components are boiling the temperature of reaction is controlled by the boiling point of the mixture at the system pressure. The heat of reaction simply creates more boil up, but no increase in temperature at a given pressure. As a result, a great deal of control over the rate of reaction and distribution of products can be achieved by regulating the system pressure. Also, adjusting the throughput (residence time = liquid hourly space velocity⁻¹) gives further control of product distribution and to a degree control of the side reactions such as oligomerization. A further benefit that this reaction may gain from catalytic distillation is the washing effect that the internal reflux provides to the catalyst thereby reducing polymer build up and coking. Internal reflux may vary over the range of 0.2 to 20 L/D (wt. liquid just below the catalyst bed/wt. distillate) give excellent results, and for the C₃-C₅ streams usually in the range of 0.5 to 4 L/D.

Quite surprisingly the low hydrogen partial pressure used in the distillation system did not result in the failure of the hydrogenation which would have been expected based on the high hydrogen partial pressure found in the liquid phase systems which are the world wide standard.

As observed earlier the phenomenon of condensation which is a constant factor in a distillation is believed to result in the same or better hydrogen availability, as the high pressure in the liquid phase, that is, the hydrogen is introduced into the liquid so that the hydrogenation occurs.

In one embodiment the present invention comprises the selective hydrogenation of acetylenic compounds and diolefins contained within a propylene rich stream to purify the stream and obtain greater amounts of the propylene. The propylene rich stream is fed to a distillation column reactor into a reaction distillation zone containing a supported palladium oxide catalyst in the form of a catalytic distillation structure. Hydrogen is provided as necessary to support the reaction and, it is believed, to reduce the oxide and maintain it in the hydride state. Previously the hydride state was believed to be the active state, however, the very low amounts of hydrogen present that give excellent results, may indicate otherwise. In any event the state of the catalyst is a matter of theory relating to mechanism, which is not the subject of the present invention. The distillation column reactor is operated at a pressure such that the reaction mixture is boiling in the bed of catalyst. If desired, a bottoms stream containing any higher boiling material may be withdrawn to effectuate a complete separation.

In a C_3 embodiment, using the hydrogen partial pressure as recited, the present invention includes a process for the selective hydrogenation of the diolefins and acetylenic compounds contained within a propylene rich stream, comprising the steps of:

(a) feeding (1) a first stream comprising propylene, di-olefins and acetylenic compounds and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;

(b) concurrently in said distillation column reactor
(i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst

capable of acting as a distillation structure thereby reacting essentially all of said diolefins and acetylenic compounds with said hydrogen to form propylene and other hydrogenated products in a reaction mixture, and

5 (ii) separating the propylene contained in said first stream and the propylene formed by the reaction of said diolefins and said acetylenic compounds from said reaction mixture by fractional distillation and

 (c) withdrawing the separated propylene from step (b)
10 (ii) along with any propane and lighter compounds, including any unreacted hydrogen, from said distillation column reactor as overheads. Optionally the process may include withdrawing any C₄ or higher boiling compounds from said distillation column reactor as bottoms. There is no
15 significant loss of propylene from the hydrogenation.

 In a C₅ embodiment, using the hydrogen partial pressure as recited, the present invention comprises feeding a light naphtha cut containing a mixture of hydrocarbons along with a hydrogen stream to a distillation column reactor
20 containing a hydrogenation catalyst which is a component of a distillation structure and selectively hydrogenating the diolefins contained in the light naphtha. Concurrently the lighter components, including the unreacted hydrogen, are distilled and separated as overheads from the partially
25 hydrogenated light naphtha product. Additionally and concurrently with the selective hydrogenation and distillation, a portion of the C₅ mono-olefins are isomerized to a more desirable feed for the production of tertiary amyl methyl ether (TAME) by the reaction of the
30 isoolefin with methanol. Essentially all of the diolefins are converted to mono olefins with very little hydrogenation of the mono-olefins.

 In a further embodiment employing the light naphtha the feed is predominately a C₅ stream and the light naphtha
35 product is withdrawn as bottoms. The overheads are passed to a condenser in which all of the condensibles are condensed and a portion refluxed to the top of the column. Reflux ratios of .5 to 20:1 may be used in the various

embodiments.

In another embodiment employing the light naphtha feed, and the hydrogen partial pressure as recited, the feed comprises a broader C₅ to C₈ stream the C₅'s are separated from the C₆+ components in the lower section of a distillation column reactor. The C₆+ components are withdrawn as a bottoms stream while the C₅'s are boiled up into the upper section of the distillation column reactor which contains the catalytic distillation structure which selectively hydrogenates the diolefins. The hydrogenated C₅'s are taken overheads along with the excess hydrogen and passed to the condenser in which all of the condensibles are condensed and subsequently separated from the uncondensibles (mostly hydrogen), for example in a reflux drum separator. A portion of the liquid from the separator is returned to the distillation column reactor as reflux and the remainder withdrawn as product which may be directly charged to a TAME unit. If desired a further inert distillation section may be utilized above the catalytic distillation structure with a C₅ product side draw below to fractionate out the excess hydrogen along with any other light components such as air, water, etc. which might be troublesome in the downstream TAME unit.

In the light naphtha embodiment the present invention is a process for the selective hydrogenation of diolefins contained in a light naphtha comprising the steps of:

(a) feeding (1) a first stream comprising a light naphtha containing diolefins and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;

(b) concurrently in said distillation column reactor

(i) contacting said first and second streams in a distillation reaction zone with a hydrogenation catalyst capable of acting as a distillation structure, thereby reacting essentially all of said diolefins with said hydrogen to form pentenes and other hydrogenated products in a reaction mixture, and

(ii) operating the pressure of the distillation

column reactor such that a portion of the mixture is vaporized by the exothermic heat of reaction;

(c) withdrawing a portion of the liquid from step (b) (ii) from said distillation column reactor as bottoms; and

5 (d) withdrawing the vapors from step (b) (ii) along with any unreacted hydrogen from said distillation column reactor as overheads.

10 The diolefins contained in the C₅ cut are higher boiling than the other compounds and therefore can be concentrated in the catalyst zone while the mono-olefins are isomerized and removed in the upper part of the column. The reactions of the C₅'s of interest are:

(1) isoprene (2-methyl butadiene-1,3) + hydrogen to 2-methyl butene-1 and 2-methyl butene-2;

15 (2) cis- and trans 1,3-pentadienes (cis and trans piperlylenes) + hydrogen to pentene-1 and pentene-2;

(3) 3-methyl butene-1 to 2-methyl butene-2 and 2-methyl butene-1;

(4) 2-methyl butene-1 to 2-methyl butene-2;

20 (5) 2-methyl butene-2 to 2-methyl butene-1; and

(5) 1,3-butadiene to butene-1 and butene-2.

The first two reactions remove the undesirable components while the third is advantageous for feed to a TAME reactor. The 3-methyl butene-1 does not react with
25 methanol to produce TAME over the sulfonic acid catalyst while the two 2-methyl butenes do.

The present invention carries out the method in a catalyst packed column which can be appreciated to contain a vapor phase and some liquid phase as in any distillation.
30 The distillation column reactor is operated at a pressure such that the reaction mixture is boiling in the bed of catalyst. The present process operates at overhead pressure of said distillation column reactor in the range between 0 and 350 psig, preferably 250 or less and
35 temperatures within said distillation reaction zone in the range of 40 to 300°F, preferably 110 to 270°F at the requisite hydrogen partial pressures. The feed weight hourly space velocity (WHSV), which is herein understood to

mean the unit weight of feed per hour entering the reaction distillation column per unit weight of catalyst in the catalytic distillation structures, may vary over a very wide range within the other condition perimeters, e.g. 0.1 to 35.

The advantages of utilizing a distillation column reactor in the instant selective hydrogenation process lie in the better selectivity of diolefin to olefin, conservation of heat and the separation by distillation which can remove some undesirable compound, e.g. heavy sulfur contaminants, from the feed prior to exposure to the catalyst and the distillation can concentrate desired components in the catalyst zone.

A "froth level" is preferably maintained throughout the catalyst bed by control of the bottoms and/or overheads withdrawal rate which improves the effectiveness of the catalyst thereby decreasing the height of catalyst needed. As may be appreciated the liquid is boiling and the physical state is actually a froth having a higher density than would be normal in a packed distillation column but less than the liquid without the boiling vapors, as described in U.S. Pat. No. 5,221,441 which is incorporated herein. Basically the froth mode called "liquid phase continuous (LPC)" hereafter is understood to mean that the flow of liquid from the catalytic distillation section has been restricted so that the rising vapor creates a froth. In effect the continuous phase is the liquid rather than the vapor as is usual in a distillation. The result is increased liquid contact with the catalytic material during the distillation and improved selective hydrogenation.

The temperature in the reactor is determined by the boiling point of the liquid mixture present at any given pressure. The temperature in the lower portions of the column will reflect the constitution of the material in that part of the column, which will be higher than the overhead; that is, at constant pressure a change in the temperature of the system indicates a change in the composition in the column. To change the temperature the

pressure is changed. Temperature control in the reaction zone is thus effected by a change in pressure; by increasing the pressure, the temperature in the system is increased, and vice versa.

5 As described the catalytic material employed in the hydrogenation process is in a form to serve as distillation packing. Broadly stated, the catalytic material is a component of a distillation system functioning as both a catalyst and distillation packing, i.e., a packing for a
10 distillation column having both a distillation function and a catalytic function.

The reaction system can be described as heterogenous since the catalyst remains a distinct entity. Any suitable hydrogenation catalyst may be used, for example Group VIII
15 metals of the Periodic Table of Elements as the principal catalytic component, alone or with promoters and modifiers such as palladium/gold, palladium/silver, cobalt/zirconium, nickel preferably deposited on a support such as alumina, fire brick, pumice, carbon, silica, resin or the like.

20 A preferred catalytic material comprises palladium oxide, preferably 0.1 to 5.0 weight %, supported on an appropriate support medium such as alumina, carbon or silica, e.g., 1/8" alumina extrudates. In a preferred catalytic distillation structure the particulate catalyst
25 material is disposed within a porous plate or screen to contain the catalyst and provide a distillation surfaces, in the form of a wire mesh structure, such as a wire mesh tubular structure or any other similar structure.

A preferred catalyst structure for the present
30 hydrogenation reaction comprising flexible, semi-rigid open mesh tubular material, such as stainless steel wire mesh, filed with a particulate catalytic material in one of several embodiments recently developed in conjunction with the present process.

35 One new catalyst structure developed for use in hydrogenations is described in US Pat. No. 5,266,546 which is incorporated herein in its entirety. Briefly the new catalyst structure is a catalytic distillation structure

comprising flexible, semi-rigid open mesh tubular material, such as stainless steel wire mesh, filed with a particulate catalytic material said tubular material having two ends and having a length in the range of from about one-half to twice the diameter of said tubular material, a first end being sealed together along a first axis to form a first seam and a second end being sealed together along a second axis to form a second seam wherein the plane of the first seam along the axis of said tubular material and the plane of the second seam along the axis of said tubular material bisect each other at an angle of about 15 to 90°.

US Patent No. 4,242,530 and US Pat. No. 4,443,559 which are incorporated herein, disclose supported catalyst in a plurality of pockets in a cloth belt or wire mesh tubular structures, which is supported in the distillation column reactor by open mesh knitted stainless steel wire by twisting the two together into a helix, which have been used. USSN 08/075,328 filed 06/11/93, which is incorporated herein, describes several other suitable structures in the prior art and disclosed new structures suitable for this process.

The particulate catalyst material may be a powder, small irregular chunks or fragments, small beads and the like. The particular form of the catalytic material in the structure is not critical, so long as sufficient surface area is provided to allow a reasonable reaction rate. The sizing of catalyst particles can be best determined for each catalytic material (since the porosity or available internal surface area will vary for different material and of course affect the activity of the catalytic material).

For the present hydrogenations the preferred catalysts structures for the packing are those employing the more open structure of permeable plates or screen wire.

Referring now to FIG. 1 there is shown a simplified flow diagram in schematic of a preferred C₅ embodiment. There is shown a distillation column reactor 10 containing a packing of suitable hydrogenation catalyst as part of a distillation structure 12, as in the wire mesh arrangement

described above. The column may also have standard distillation structure 14. The light naphtha is fed via line 1 to the distillation column reactor 10 below the catalyst packing. The hydrogen is fed as a gas via flow line 2 at or near the bottom of the bed of catalyst packing.

The C₅ feed and the hydrogen are preferably fed to the distillation column reactor separately or they may be mixed prior to feeding. A mixed feed is fed below the catalyst bed or at the lower end of the bed. Hydrogen alone is fed below the catalyst bed and the C₅ stream is preferably fed below the bed. Although hydrocarbon is preferably fed below the bed to keep out heavy impurities such as sulfur compounds, it may be fed up to the mid one-third of the bed. The pressure selected is that which maintains the dienes and other highly unsaturated compounds in the catalyst bed while allowing the propylene and lighter to distill overhead.

Heat is added to the bottoms via flow line 4 by circulating through the reboiler 40 and back to the column via flow line 13. After the reaction has started the heat of reaction, which is exothermic, causes additional vaporization of the mixture in the bed. Vapors are taken overhead through flow line 3 and passed to condenser 20 where substantially all of the condensible material is condensed to a temperature of 100°F. The overheads are then passed to reflux drum 30 where the condensed material is collected and separated from uncondensibles, such as the unreacted hydrogen. A portion of the condensed materials collected in the reflux drum are returned to the top of the distillation column reactor 10 via flow line 6. The distillate product, withdrawn through line 9, is a suitable feed for a TAME reactor. The uncondensable material is vented from the reflux drum via flow line 7 and for economy the hydrogen can be recycled to the reactor (not shown).

Bottoms product containing essentially no C₅ diolefins is withdrawn via flow line 8 and may be sent to gasoline

blending as stable gasoline. The process is advantageous because the high heat of hydrogenation is absorbed by the vaporization of part of the liquid, so temperature control is achieved by adjusting the system pressure. All excess hydrogen is stripped from the bottoms product. In the case of C₅'s, the unhydrogenated components are less volatile and tend to stay in the reactor for a longer time assisting in more complete reaction.

In FIG. 2 there is shown a second embodiment of the invention wherein the light naphtha is fed to the column 10 above the catalytic distillation structure 12 via flow line 1'. Otherwise the arrangement is identical to FIG. 1. FIG. 3 illustrates a third embodiment wherein the column includes additional conventional distillation structure 216 above the catalytic distillation structure 12 to separate any C₄ and lighter material, hydrogen, and other lower boiling components from the C₅'s which are withdrawn as side stream via flow line 209.

Example 1

In this example the hydrocarbon stream is rich in propylene such as a C₃ cut from the gas plant of a fluid catalytic cracking unit or a steam cracker. A typical analysis of such a stream is given in Table II below.

The catalyst is 0.3 wt% PdO on 1/8" Al₂O₃ (alumina) extrudates, hydrogenation catalyst, supplied by United Catalysts, Inc. designated as G68F. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE I

30	Designation	G68F
	Form	spheres
	Nominal size	3x6 Mesh
	Pd. wt%	0.3
	Support	High purity alumina

35 The catalyst is believed to be the hydride of palladium which is produced during operation.

The hydrogen rate to the reactor must be sufficient to maintain the catalyst in the active form because hydrogen

is lost from the catalyst by hydrogenation. The hydrogen rate must be adjusted at the partial pressure described such that it is sufficient to support the hydrogenation reaction and replace hydrogen lost from the catalyst but
 5 kept below that required for hydrogenation of propylene and to prevent flooding of the column. Generally the mole ratio of hydrogen to acetylenic compounds in the feed to the fixed bed of the will be about 1.05 to 2.5 preferably 1.4 to 2.0. The presence of hydrogen feed as described
 10 herein does not adversely effect the physical operation of the catalytic distillation system.

TABLE II

	Component	Mole Per cent
	Methane	0.000
15	Ethylene	0.000
	Ethane	0.075
	Propylene	82.722
	Propane	11.118
	Methyl Acetylene	2.368
20	Propadiene	1.304
	Cyclo C ₃	0.048
	Isobutane	0.000
	Isobutene	0.015
	Butene-1	0.242
25	Butadiene	1.529
	Normal butane	0.112
	Trans butene-2	0.008
	Vinyl acetylene	0.013
	Cis butene-2	0.000
30	C ₅ 's and heavier	0.000
	Total	100.000
	Propylene/Propane	7.440

The propylene containing feed and the hydrogen may be fed to the distillation column reactor separately or they
 35 may be mixed prior to feeding. A mixed feed is fed below the catalyst bed or at the lower end of the bed. Hydrogen alone is fed below the catalyst bed and the C₃ stream is preferably fed below the bed. Hydrocarbon fed into the bed

can result in some catalyst being deactivated by the impurities. The pressure selected is that which maintains the dienes and acetylenes in the catalyst bed while allowing the propylene and lighter to distill overhead.

5 Any unreacted hydrogen exits overhead with the C₃'s.

The pilot unit used was a 1 inch laboratory column fifteen feet in height. The catalyst, 240 grams of 0.3 wt% PdO on 1/8 inch alumina extrudates) was placed in pouches of distillation wire mesh packing to form the catalytic
10 distillation structures described in the U.S. Pat.No. 5,266,546 incorporated herein. The catalytic distillation structures were loaded into the middle ten feet of the column with the lower and upper 2.5 feet filled with inert distillation packing. The propylene rich feed and hydrogen
15 were started to the column and heat added to initiate the reaction. The overhead pressure was maintained at between 240 and 315 psig. In the pilot unit no bottoms were taken, and an equilibrium amount of C₄'s + of about 15 vol% was present in the lower section of the column as indicated by
20 a constant temperature of about 140°F. The constant temperature also indicated that no build up of heavier materials occurred as a result of any oligomerization. If there were any residual diene the bottoms temperature would have increased as the heavies built up, thus indicating
25 total selective removal of the dienes and acetylenes. In commercial or larger scale units a bottoms draw would probably be included to effectuate the separation of the C₄'s + from the propylene product. Table III below gives the results from the pilot unit run.

Example 2

The catalyst is 0.34 wt% Pd on 3 to 8 mesh Al_2O_3 (alumina) spheres, supplied by United Catalysts Inc. designated as G68C. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE IV

	Designation	G68C
	Form	Sphere
10	Nominal size	5x8 mesh
	Pd. wt%	0.3 (0.27-0.33)
	Support	High purity alumina

The catalyst is believed to be the hydride of palladium which is produced during operation. The hydrogen rate to the reactor must be sufficient to maintain the catalyst in the active form because hydrogen is lost from the catalyst by hydrogenation. The "effectuating amount of hydrogen " as that term is used herein as regards the C_5 's will be at least 1.0 to 1.0 preferably over 2.0 to 1.0, for example about 10:1 moles of hydrogen per mole of diolefin.

A three inch diameter 30 foot tall steel column 310 with a reboiler 340, condenser 320 and reflux system 330 and 306 is used as shown in FIG. 4. The middle 15 feet are packed with a catalytic distillation structure 312 comprising 0.34 wt% palladium on 1/8 inch alumina spherical catalyst which is contained in the pockets of a fiber glass belt and twisted with stainless steel wire mesh. The column is purged with nitrogen and pressure up to 20 psig. Light naphtha feed which has been prefractionated to remove most of the C_6+ material is started to the column via line 301 at 50 lbs/hr. When a bottom level is obtained and the liquid is at the desired level in the column, bottoms draw through line 308 is started and reboiler circulation began through line 304 and 313. Heat is added to the reboiler 340 until vapor is seen at the top of the column as evidenced by a uniform temperature of 130°F throughout the column. Hydrogen flow is started to the bottom of the column at between 8 to 10 SCFH via line 302. The pressure

on the column is then controlled to maintain a bottoms temperature of about 320°F and a catalyst bed temperature of about 260°F. The overhead pressure was thus maintained about 200 psig. The overheads are taken via line 303 and partially condensed in condenser 320 and all of the condensibles collected in reflux drum 330 and returned to the top of the column as reflux via line 306. Uncondensibles are vented from the drum via line 307. Liquid bottoms are withdrawn via line 308. The results are shown in TABLE V below in which the feed and bottoms analyses are compared.

TABLE V

Component, wt%	Feed	Bottoms Product	% Change
Lights	0.073	0.000	-100
Dimethyl ether	0.003	0.002	-36
isobutane	0.488	0.093	-81
methanol	0.058	0.000	-100
Other C ₄ 's	4.573	3.304	-28
3-methyl butene-1	1.026	0.270	-74
isopentane	31.974	32.066	0
pentene-1	2.708	0.962	-64
2-methyl butene-1	6.496	4.012	-38
normal pentane	3.848	4.061	6
2-methyl butadiene-1,3	0.147	0.002	-99
trans pentene-2	6.995	9.066	30
Unknown 1	0.138	0.094	-32
cis pentene-2	3.886	3.723	-4
2-methyl butene-2	11.634	14.083	21
trans piperylene	0.142	0.002	-98
cis piperylene	0.095	0.003	-97
cyclo-C ₅	0.001	0.058	-47
C ₆ +	<u>25.603</u>	<u>28.198</u>	10
Total	100.000	100.000	

Example 3

During the run of Example 2 the overhead pressure was adjusted to vary the catalyst bed temperature. At lower temperatures the conversion of the diolefins was lower, but the main difference was that the isomerization of the 3-methyl butene-1 was more dramatically affected. Table VI below compares the conversions of the diolefins and 3-methyl butene-1 with the operating temperature.

TABLE VI

Mid. Temp °F	OH Press psig	Hrs on STM	Conversion, Mole %			
			<u>isoprene</u>	<u>t-Pip</u>	<u>c-Pip</u>	<u>3-methyl butene-1</u>
230	130	200	65	57	65	17
250	145	300	97	95	95	55
265	200	600	100	99	99	80

Example 4

C₄ STREAMS

This set of runs demonstrates the unexpected diene removal from C₄ streams at extremely low hydrogen partial pressures. It was also demonstrated that lower total pressures were also suitable. The runs were conducted in two modes. In one mode, conventional distillation, a vapor continuous phase was used. In the other mode, a preferred liquid continuous phase "LPC" mode was used.

The reactor used for Run 1 was a three inch diameter column containing 20 feet of catalyst packing, containing 1 cubic foot of catalytic material (0.5% pd on 8-12 mesh alumina-E144SDU product of Calcat, Catalyst and Performance Chemicals Division, Mallinckrodt, Inc.), with 4.5 feet of 5/8" steel pall rings above and 15.5 feet of 5/8" steel Pall rings below the catalyst bed. Run 2 used a three inch diameter column containing 20 feet of catalyst packing, containing 1 cubic foot of catalytic material (0.5% pd on 8-12 mesh alumina-E144SDU product of Calcat, Catalyst and Performance Chemicals Division, Mallinckrodt, Inc.), with 4.5 feet of 5/8" steel pall rings above and 25

feet of demister wire and 50 feet of 5/8" steel Pall rings below the catalyst bed. The catalyst was loaded into tubular one inch wire casings positioned diagonally on demister wire and rolled into a bale of about 3" diameter.

5 The hydrocarbon is fed to the column below the catalyst. To start up the overhead pressure is set to 120 psig and the reboiler is charged with hydrocarbon fed at about 20 pounds per hour with the reboiler set at 10% which is maintained for 15 minutes at which time the feed rate is
10 adjusted to maintain 50-75% bottoms level until the overhead temperature is within 20 degrees of the bottoms temperature then increase the hydrocarbon feed rate to 100 lb/hr. When the differential pressure reaches 1.0 psi the hydrogen flow is initiated at 15 scfh. Bottoms are
15 heated to a uniform temperature of 160° F then a mid reflux flow is started. The overhead pressure is selected and the reaction distillation is carried out. The C₄ hydrocarbon feed conditions and results for each run are set out in TABLES VII and VIII.

20 Runs carried out in the LPC mode removed all of the dienes whereas conventional distillation left a few parts per million under the same conditions. The internal reflux rate is reported as the ratio of the liquid immediately below the catalyst packing to the distillate (L/D). The
25 data shows the LPC mode to give better diene removal.

TABLE VII
EXAMPLE 4-RUN 1-part 1

HOURS ON LINE 41CONDITIONS

Hydrogen pp psia	2.3
Feed Source	Refinery FCC
Feed Rate lb/hr	100
H ₂ Rate scfh	15
Pressure, psig	120
Distillate lb/hr	93
Internal Reflux Rate	0.73
Mode	Conventional

RESULTS

Analysis	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Ethylene	0.02	0.01	0.00	0.00
Ethane	0.20	0.01	0.00	0.69
Propylene	0.27	0.22	0.00	2.61
Propane	0.48	0.44	0.00	3.34
Isobutane	31.38	32.63	0.18	31.70
Isobutene	14.21	14.77	0.74	11.41
Butene-1	12.82	4.59	1.07	3.25
1,3-Butadiene	0.2788	0.0030	0.0199	0.0000
N-Butane	9.37	10.13	8.55	4.95
Trans-butene-2	17.13	24.69	25.56	11.49
2,2-Dimethylpropane	0.00	0.00	0.08	
Methylcyclopropane	0.02	0.02	0.02	
Cis-butene-2	12.50	12.20	53.01	4.91
C ₅ 's	1.26	0.27	10.58	0.06
Heavies	0.01	0.01	0.18	0.21
Total	100.00	100.0	100.0	
lbs/hr	100.0	93.0	5	1.8
Temp. °F		155	188	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.28	30 ppm
Isobutane	31.4	31.0
N-Butenes	42.5	43.0
N-Butane	9.4	10.0
% Butene-1 of total N-Butenes	30.2	10.2

TABLE VII (CONTINUED)
EXAMPLE 4-RUN 1-part 2

HOURS ON LINE 102CONDITIONS

Hydrogen pp psia	1.5
Feed Source	Refinery FCC
Feed Rate lb/hr	100
H ₂ Rate scfh	10
Pressure, psig	120
Distillate lb/hr	93
Internal Reflux Rate	0.74
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Ethylene	0.02	0.01	0.00	0.00
Ethane	0.20	0.02	0.00	0.70
Propylene	0.27	0.25	0.00	2.13
Propane	0.48	0.47	0.00	2.52
Isobutane	31.38	32.97	0.21	23.22
Isobutene	14.21	14.82	0.81	8.18
Butene-1	12.82	3.67	1.15	1.92
1,3-Butadiene	0.2788	0.0000	0.0211	0.0000
N-Butane	9.37	9.93	8.84	3.43
Trans-butene-2	17.13	25.37	25.71	8.29
2,2-Dimethylpropane	0.00	0.00	0.08	
Methylcyclopropane	0.02	0.02	0.02	
Cis-butene-2	12.50	12.20	52.25	3.46
C ₅ 's	1.26	0.28	10.70	0.00
Heavies	0.01	0.00	0.20	0.00
Total	100.00	100.0	100.00	
lbs/hr	100.0	93.1	5	2.0
Temp. °F		155	188	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.28	0 ppm
Isobutane	31.4	31.2
N-Butenes	42.5	42.6
N-Butane	9.4	9.8
% Butene-1 of total N-Butenes	30.2	8.2

TABLE VII (CONTINUED)
EXAMPLE 4-RUN 1-part 3

HOURS ON LINE 161CONDITIONS

Hydrogen pp psia	0.8
Feed Source	Refinery FCC
Feed Rate lb/hr	100
H ₂ Rate scfh	5
Pressure, psig	120
Distillate lb/hr	93
Internal Reflux Rate	0.74
Mode	Conventional

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Ethylene	0.02	0.01	0.00	0.00
Ethane	0.20	0.01	0.00	0.64
Propylene	0.27	0.25	0.00	1.96
Propane	0.48	0.46	0.00	2.24
Isobutane	31.38	32.84	0.47	20.08
Isobutene	14.21	14.87	0.87	7.12
Butene-1	12.82	10.32	1.20	4.26
1,3-Butadiene	0.2788	0.0262	0.0227	0.0000
N-Butane	9.37	9.52	8.71	2.87
Trans-butene-2	17.13	19.35	25.66	5.71
2,2-Dimethylpropane	0.00	0.00	0.08	
Methylcyclopropane	0.02	0.02	0.02	
Cis-butene-2	12.50	12.08	52.60	2.96
C ₅ 's	1.26	0.24	10.23	0.00
Heavies	0.01	0.00	0.12	0.00
Total	100.00	100.0	100.00	
lbs/hr	100.0	92.7	5	2.3
Temp. °F		156	188	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.28	262 ppm
Isobutane	31.4	30.9
N-Butenes	42.5	43.0
N-Butane	9.4	9.3
% Butene-1 of total N-Butenes	30.2	22.6

TABLE VII (CONTINUED)
EXAMPLE 4-RUN 1-part 4

HOURS ON LINE 198CONDITIONS

Hydrogen pp psia	1.5
Feed Source	Refinery FCC
Feed Rate lb/hr	100
H ₂ Rate scfh	10
Pressure, psig	120
Distillate lb/hr	93
Internal Reflux Rate	0.74
Mode	Conventional

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vents wt %
Ethylene	0.02	0.01	0.00	0.00
Ethane	0.20	0.01	0.02	0.64
Propylene	0.27	0.25	0.03	2.08
Propane	0.48	0.46	0.05	2.42
Isobutane	31.38	32.97	3.92	20.74
Isobutene	14.21	14.90	2.43	7.27
Butene-1	12.82	7.29	2.61	3.26
1,3-Butadiene	0.2788	0.0105	0.0509	0.0000
N-Butane	9.37	9.64	8.81	2.90
Trans-butene-2	17.13	21.91	24.64	6.32
2,2-Dimethylpropane	0.00	0.00	0.07	
Methylcyclopropane	0.02	0.02	0.02	
Cis-butene-2	12.50	12.29	47.97	2.97
C'5's	1.26	0.23	9.22	0.00
Heavies	0.01	0.01	0.17	0.00
Total	100.00	100.0	100.00	
lbs/hr	100.0	93.0	5	2.1
Temp. °F		155	188	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.28	105 ppm
Isobutane	31.4	31.3
N-Butenes	42.5	42.6
N-Butane	9.4	9.5
% Butene-1 of total N-Butenes	30.2	16.4

TABLE VIII
EXAMPLE 4-RUN 2-part 1

HOURS ON LINE 138CONDITIONS

Hydrogen pp psia	1.5
Feed Source	Refinery FCC
Feed Rate lb/hr	56
H ₂ Rate scfh	15
Pressure, psig	125
Distillate lb/hr	37
Internal Reflux Rate	4.72
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Ethylene	0.03	0.03	0.00	0.00
Ethane	0.22	0.11	0.00	0.14
Propylene	0.24	0.31	0.00	0.68
Propane	0.53	0.68	0.00	1.18
Isobutane	28.17	39.45	0.01	33.16
Isobutene	15.05	21.03	0.0032	16.91
Butene-1	13.91	7.81	0.01	5.99
1,3-Butadiene	0.3441	0.0000	0.0000	0.0000
N-Butane	8.65	7.34	12.86	5.04
Trans-butene-2	17.76	16.71	40.71	11.43
2,2-Dimethylpropane	0.00	0.00	0.04	
Methylcyclopropane	0.02	0.01	0.03	
Cis-butene-2	13.55	6.51	40.84	4.26
C ₅ 's	1.53	0.02	5.47	0.00
Heavies	0.00	0.00	0.01	0.05
Total	100.00	100.0	100.00	
lbs/hr	56.0	37.1	15	4.0
Temp. °F		164	182	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.3	0 ppm
Isobutane	28.2	28.5
N-Butenes	45.2	43.9
N-Butane	8.7	8.7
% Butene-1 of total N-Butenes	30.8	12.8

TABLE VIII
EXAMPLE 4-RUN 2-part 2

HOURS ON LINE 173CONDITIONS

Hydrogen pp psia	1.5
Feed Source	Refinery FCC
Feed Rate lb/hr	56
H ₂ Rate scfh	15
Pressure, psig	125
Distillate lb/hr	32
Internal Reflux Rate	5.46
Mode	LPC

RESULTS

Analysis	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Ethylene	0.03	0.03	0.00	0.02
Ethane	0.22	0.09	0.00	0.29
Propylene	0.24	0.33	0.00	0.77
Propane	0.53	0.74	0.00	2.56
Isobutane	28.17	43.97	0.01	43.60
Isobutene	15.05	23.39	0.0541	5.45
Butene-1	13.91	7.20	0.22	19.75
1,3-Butadiene	0.3441	0.0000	0.0024	0.0000
N-Butane	8.65	5.24	15.64	3.88
Trans-butene-2	17.76	13.92	42.32	8.80
2,2-Dimethylpropane	0.00	0.00	0.03	
Methylcyclopropane	0.02	0.01	0.03	
Cis-butene-2	13.55	5.07	37.33	3.22
C ₅ 's	1.53	0.00	4.35	0.00
Heavies	0.00	0.00	0.01	0.00
Total	100.00	100.0	100.00	
lbs/hr	56.0	32.2	19	4.9
Temp. °F		164	182	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.3	0 ppm
Isobutane	28.2	29.1
N-Butenes	45.2	44.9
N-Butane	8.7	8.6
% Butene-1 of total N-Butenes	30.8	13.3

Example 5

LIGHT FCC NAPHTHA STREAMS

The same procedures as set out in Example 4 were used, however the catalyst was G68C-1, a 0.4% palladium on 7-12 mesh alumina product of United Catalyst, Inc. Thirty feet of catalyst packing (1.5 cubic foot of catalytic material) prepared as a distillation structure as described in Example 4 was loaded in a three inch column, with 5 feet of 5/8" steel pall rings and 10 feet of open space above and 3 feet of demister wire and 50 feet of 5/8" steel pall rings below. The distillation was conducted to take hydrotreated C₅'s overhead and the heavier components as bottoms. The feeds, conditions and results for each of three runs are set out in TABLES IX-XI.

The results of Run 3 at 74 hours on stream which was carried out at low hydrogen partial pressure and high 20 WHSV were below expectations. By increasing the hydrogen partial pressure to only 4.4 psia at 272 hours on stream in a conventional distillation mode the diene removal was improved 10 fold.

TABLE IX
EXAMPLE 5-RUN 1HOURS ON LINE 99CONDITIONS

Hydrogen pp, psia	4.5
Feed Rate, lb/hr	219
H ₂ Rate, scfh	20
Pressure, psig	125
Distillate, lb/hr	47
Internal Reflux Rate	2.11
Mode	LPC

RESULTS

Analysis	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
C ₄ 's	0.00	0.00	0.00	
Isobutane	0.00	0.02	0.00	0.02
Other C ₄ 's	0.33	1.52	0.04	
3-Methyl Butene-1	0.28	0.27	0.06	
Isopentane	7.40	32.40	2.32	33.23
Pentene-1	1.07	1.47	0.34	
2-Methyl Butene-1	1.81	4.09	0.60	
N-Pentane	3.82	17.65	1.62	
2-Methyl Butadiene-1,3	0.1761	0.0000	0.0595	
Trans-Pentene-2	2.45	14.99	1.02	
Unknown 1	0.02	0.04	0.02	
Cis-Pentene-2	1.36	4.86	0.59	21.62
2-Methyl Butene-2	3.28	17.93	1.69	
Trans-Piperylene	0.18	0.00	0.10	
Cis-Piperylene	0.06	0.00	0.04	
Cyclopentene	0.29	0.26	0.26	
Unknowns 2	5.12	4.12	11.26	
Heavies	72.36	0.38	79.97	
Total	100.00	100.0	100.00	
lbs/hr	218.8	47.0	171.9	0.00
Temp. °F		256	417	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	1.91	17 ppm
2MB1 + 2MB2	22.9	24.2
Isopentane	33.4	32.5
Pentenenes	22.0	22.6
N-Pentane	17.2	18.8
% 3-MB-1 of total		
Isoamylenes	5.23	1.63
% Pentene-1 of		
total N-Pentenenes	22.0	9.5

TABLE X
EXAMPLE 5-RUN 2-page 1

HOURS ON LINE 45CONDITIONS

Hydrogen pp, psia	4.8
Feed Rate, lb/hr	217
H ₂ Rate, scfh	20
Pressure, psig	125
Distillate, lb/hr	42
Internal Reflux Rate	2.22
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
C ₄ 's	0.00	0.00	0.00	
Isobutane	0.03	0.16	0.00	0.32
Other C ₄ 's	1.46	7.33	0.00	
3-Methyl Butene-1	0.21	0.20	0.00	
Isopentane	7.85	38.92	0.08	34.49
Pentene-1	0.76	1.04	0.02	
2-Methyl Butene-1	1.37	3.08	0.06	
N-Pentane	3.56	13.79	0.73	
2-Methyl Butadiene-1,3	0.101	0.0000	0.0110	
Trans-Pentene-2	2.08	10.77	0.42	
Unknown 1	0.02	0.04	0.01	
Cis-Pentene-2	1.15	3.50	0.29	16.97
2-Methyl Butene-2	2.87	13.90	0.91	
Trans-Piperylene	0.11	0.00	0.04	
Cis-Piperylene	0.04	0.00	0.01	
Cyclo-C ₅	0.31	0.43	0.23	
Unknowns 2	6.49	6.01	6.46	
Heavies	71.58	0.83	90.71	
Total	100.00	100.00	100.00	
lbs/hr	217.3	41.9	175.4	0.00
Temp. °F		260	406	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	1.21	0 ppm
2MB1 + 2MB2	20.8	21.6
Isopentane	38.4	40.3
Pentenenes	19.6	18.9
N-Pentane	17.4	17.3
% 3-MB-1 of total		
Isoamylenes	4.80	0.94
% Pentene-1 of		
total N-Pentenenes	19.0	6.1

TABLE X (CONTINUED)
EXAMPLE 5-RUN 2-page 2

HOURS ON LINE 201CONDITIONS

Hydrogen pp, psia	2.9
Feed Rate, lb/hr	219
H ₂ Rate, scfh	20
Pressure, psig	75
Distillate, lb/hr	41
Internal Reflux Rate	2.50
Mode	LPC

RESULTS

Analysis	Feed wt %	Overhead wt %	Bottoms wt %	Vents wt %
C ₄ 's	0.00	0.02	0.00	
Isobutane	0.03	0.15	0.00	0.30
Other C ₄ 's	1.48	6.85	0.00	
3-Methyl Butene-1	0.21	0.32	0.00	
Isopentane	7.85	36.28	0.03	42.53
Pentene-1	0.76	1.18	0.01	
2-Methyl Butene-1	1.37	3.94	0.04	
N-Pentane	3.56	15.98	0.58	
2-Methyl Butadiene-1,3	0.1013	0.0000	0.0085	
Trans-Pentene-2	2.08	12.08	0.33	
Unknown 1	0.02	0.05	0.00	
Cis-Pentene-2	1.15	3.88	0.23	18.14
2-Methyl Butene-2	2.87	13.81	0.76	
Trans-Piperylene	0.11	0.00	0.04	
Cis-Piperylene	0.04	0.00	0.01	
Cyclo-C ₅	0.31	0.42	0.20	
Unknowns 2	6.49	4.49	6.35	
Heavies	71.58	0.54	91.42	
Total	100.00	100.00	100.00	
lbs/hr	219.0	41.0	175.7	2.6
Temp. °F		212	359	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	1.21	0 ppm
2MB1 + 2MB2	20.8	20.9
Isopentane	38.4	38.6
Pentenenes	19.6	20.5
N-Pentane	17.4	18.2
% 3-MB-1 of total		
Isoamylenes	4.80	1.50
% Pentene-1 of total N-Pentenenes	19.0	6.0

TABLE XI
EXAMPLE 5-RUN 3-page 1

HOURS ON LINE 44CONDITIONS

Hydrogen pp, psia	2.7
Feed Rate, lb/hr	295
H ₂ Rate, scfh	20
Pressure, psig	100
Distillate, lb/hr	55
Internal Reflux Rate	2.65
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
C ₄ 's	0.02	0.07	0.00	
Isobutane	0.07	0.27	0.00	0.49
Other C ₄ 's	1.41	0.00	0.00	
3-Methyl Butene-1	0.25	0.73	0.00	
Isopentane	8.66	36.35	0.20	26.57
Pentene-1	0.87	2.09	0.02	
2-Methyl Butene-1	1.83	6.60	0.05	
N-Pentane	1.51	6.42	0.12	
2-Methyl Butadiene-1,3	0.0537	0.0024	0.0000	
Trans-Pentene-2	2.58	13.00	0.21	
Unknown 1	0.03	0.07	0.02	
Cis-Pentene-2	1.42	5.13	0.22	28.45
2-Methyl Butene-2	3.93	15.45	1.12	
Trans-Piperylene	0.06	0.00	0.02	
Cis-Piperylene	0.03	0.00	0.01	
Cyclo-C ₅	0.06	0.05	0.04	
Unknowns 2	7.50	6.65	7.69	
Heavies	69.71	7.12	90.28	
Total	100.00	100.00	100.00	
lbs/hr	294.9	55.0	236.9	3.1
Temp. °F		240	388	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.68	53 ppm
2MB1 + 2MB2	27.1	27.7
Isopentane	40.7	39.7
Pentenes	22.9	24.4
N-Pentane	7.1	7.1
% 3-MB-1 of total		
Isoamylenes	4.23	2.61
% Pentene-1 of		
total N-Pentenes	17.8	9.2

TABLE XI (CONTINUED)
EXAMPLE 5-RUN 3-page 2

HOURS ON LINE 74CONDITIONS

Hydrogen pp, psia	1.5
Feed Rate, lb/hr	295
H ₂ Rate, scfh	10
Pressure, psig	100
Distillate, lb/hr	52
Internal Reflux Rate	2.56
Mode	LPC

RESULTS

Analysis	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
C ₄ 's	0.02	0.08	0.00	
Isobutane	0.07	0.29	0.00	0.68
Other C ₄ 's	1.41	6.44	0.00	
3-Methyl Butene-1	0.25	1.13	0.00	
Isopentane	8.66	39.14	0.20	32.86
Pentene-1	0.87	3.65	0.02	
2-Methyl Butene-1	1.83	8.35	0.05	
N-Pentane	1.51	5.84	0.12	
2-Methyl Butadiene-1,3	0.0537	0.0417	0.0000	
Trans-Pentene-2	2.58	10.45	0.21	
Unknown 1	0.03	0.07	0.02	
Cis-Pentene-2	1.42	5.11	0.22	0.00
2-Methyl Butene-2	3.93	13.09	1.12	
Trans-Piperylene	0.06	0.03	0.02	
Cis-Piperylene	0.03	0.05	0.01	
Cyclo-C ₅	0.06	0.06	0.04	
Unknowns 2	7.50	5.29	7.69	
Heavies	69.71	0.90	90.28%	
Total	100.00	100.00	100.00	
lbs/hr	295.1	52.0	241.2	2.0
Temp. °F		236	383	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.68	1263 ppm
2MB1 + 2MB2	27.1	27.5
Isopentane	40.7	42.4
Pentenes	22.9	21.9
N-Pentane	7.1	6.5
% 3-MB-1 of total		
Isoamylenes	4.23	4.02
% Pentene-1 of		
total N-Pentenes	17.8	17.6

TABLE XI (CONTINUED)
EXAMPLE 5-RUN 3-page 3

HOURS ON LINE 272CONDITIONS

Hydrogen pp, psia	4.4
Feed Rate, lb/hr	295
H ₂ Rate, scfh	30
Pressure, psig	100
Distillate, lb/hr	53
Internal Reflux Rate	2.43
Mode	Conventional

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vents wt %
C ₄ 's	0.02	0.08	0.00	
Isobutane	0.07	1.03	0.00	1.58
Other C ₄ 's	1.41	11.21	0.00	
3-Methyl Butene-1	0.25	0.91	0.00	
Isopentane	8.66	42.05	0.60	26.14
Pentene-1	0.87	2.11	0.14	
2-Methyl Butene-1	1.83	6.24	0.36	
N-Pentane	1.51	5.06	0.63	
2-Methyl Butadiene-1,3	0.0537	0.0057	0.0000	
Trans-Pentene-2	2.58	9.32	0.98	
Unknown 1	0.03	0.06	0.02	
Cis-Pentene-2	1.42	3.98	0.60	18.29
2-Methyl Butene-2	3.93	11.56	1.87	
Trans-Piperylene	0.06	0.00	0.03	
Cis-Piperylene	0.03	0.01	0.01	
Cyclo-C ₅	0.06	0.04	0.04	
Unknowns 2	7.50	5.29	13.06	
Heavies	69.71	1.11	81.65	
Total	100.00	100.00	100.00	
lbs/hr	295.0	53.0	238.1	4.00
Temp. °F		233	369	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	0.68	126 ppm
2MB1 + 2MB2	27.1	25.7
Isopentane	40.7	43.1
Pentenes	22.9	22.6
N-Pentane	7.1	7.3
% 3-MB-1 of total		
Isoamylenes	4.23	3.17
% Pentene-1 of		
total N-Pentenes	17.8	11.2

EXAMPLE 6

C₃ STREAMS

The same procedures as set out in Example 4 were used, however the catalyst in Run 1 was G68C, a 0.3% palladium on 3-6 mesh alumina product of United Catalyst, Inc. Twenty
5 feet of catalyst packing (1.0 cubic foot of catalytic material) prepared as distillation structures as described in U.S. Pat No. 5,266,546, which are tubular wire mesh about 2" long with 2" diameter having the ends sealed at 90° to each other. The catalyst packing was loaded in a
10 three inch column, with 5 feet of 5/8" steel pall rings and 10 feet of open space above and 3 feet of demister wire and 50 feet of 5/8" steel pall rings below. The same structures and column was used in Run 2, but the catalyst was United Catalyst G68H (0.3% Pd and 0.3% Ag on alumina)

15 The distillation was conducted to take hydrotreated C₅'s overhead and the heavier components as bottoms. The feeds, conditions and results for each of three runs are set out in TABLEs XII and XIII.

TABLE XII
EXAMPLE 6-RUN 1HOURS ON LINE 213CONDITIONS

Hydrogen pp, psia	6.4
Feed Rate, lb/hr	90
H ₂ Rate, scfh	34
Pressure, psig	250
Distillate, lb/hr	82
Internal Reflux Ratio	0.88
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Methane	0.00	0.00	0.00	0.06
Ethylene	0.00	0.00	0.00	0.45
Ethane	0.05	0.03	0.00	
Propene	85.43	88.88	22.85	78.94
Propane	9.93	11.02	8.81	7.20
Methylacetylene	1.99	0.0000	7.66	
Propadiene	0.81	0.0000	5.45	
Cyclopropane	0.05	0.04	0.34	
Isobutane	0.00	0.00	0.10	
Isobutene	0.01	0.00	0.27	
Butene-1	0.21	0.00	6.30	0.13
Butadiene	1.37	0.00	25.59	
N-butane	0.00	0.00	2.56	
Vinylacetylene	0.00	0.00	0.22	
Trans-butene-2	0.01	0.00	2.34	
Cis-butene-2	0.01	0.00	1.12	
C ₅ 's	0.04	0.00	0.75	0.04
C ₆ 's	0.00	0.00	13.51	
Heavies	0.00	0.00	0.01	0.05
Total	100.00	100.0	100.00	
lbs/hr	56.0	37.1	15	4.1
Temp. °F		113	216	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	4.2	0 ppm
Propylene	85.4	85.8
Propane	9.9	10.8
C ₆	0.06	0.65

TABLE XIII
EXAMPLE 6-RUN 2HOURS ON LINE 152CONDITIONS

Hydrogen pp, psia	5.2
Feed Rate, lb/hr	90
H ₂ Rate, scfh	34
Pressure, psig	250
Distillate, lb/hr	84
Internal Reflux Ratio	1.27
Mode	LPC

RESULTS

Analysis

	Feed wt %	Overhead wt %	Bottoms wt %	Vent wt %
Methane	0.00	0.00	0.00	0.01
Ethylene	0.00	0.00	0.00	0.54
Ethane	0.05	0.03	0.00	
Propene	85.43	88.94	22.17	74.14
Propane	9.93	10.12	10.13	6.47
Methylacetylene	1.99	0.0000	8.70	
Propadiene	0.81	0.0000	5.90	
Cyclopropane	0.05	0.03	0.43	
Isobutane	0.00	0.00	0.39	
Isobutene	0.01	0.00	0.34	
Butene-1	0.21	0.00	6.08	0.13
Butadiene	1.37	0.00	30.57	
N-butane	0.00	0.00	3.02	
Vinylacetylene	0.00	0.00	0.25	
Trans-butene-2	0.01	0.00	0.70	
Cis-butene-2	0.01	0.00	0.22	
C ₅ 's	0.04	0.00	0.83	0.04
C ₆ 's	0.00	0.00	8.76	
Heavies	0.05	0.02	1.52	
Total	100.00	100.0	100.00	
lbs/hr	90.0	83.9	3.5	2.8
Temp. °F		113	171	

COMPONENT SUMMARY

Component	Feed wt %	Product wt %
Dienes	4.2	0 ppm
Propylene	85.4	86.1
Propane	9.9	10.0
C ₆	0.06	0.42

The invention claimed is:

1. A process for the selective hydrogenation of highly unsaturated compounds comprising feeding a hydrocarbon stream containing highly unsaturated compounds which comprise diolefins and acetylenes along with a hydrogen stream at an effectuating hydrogen partial pressure in the range of least about 0.1 psia to less than 70 psia to a distillation column reactor containing a hydrogenation catalyst which is a component of a distillation structure and selectively hydrogenating a portion of the highly unsaturated compounds.

2. The process according to claim 1 wherein said hydrocarbon stream comprises aliphatic compounds having three to nine carbon atoms.

3. The process according to claim 1 wherein said hydrocarbon stream comprises a major amount of normal olefins which are recovered as products from said hydrogenation.

4. The process according to claim 1 wherein said hydrocarbon has a WHSV in the range of 0.1 to 35.

5. The process according to claim 2 wherein the overhead pressure is in the range of 0 to 350 psig.

6. The process according to claim 1 wherein the hydrogen partial pressure is less than 50 psia.

7. The process according to claim 6 wherein the hydrogen partial pressure is less than 10 psia.

8. The process according to claim 7 wherein the hydrogen partial pressure is less than 7 psia.

9. The process according to claim 5 wherein said hydrogen partial pressure is less than 50 psia.

10. The process according to claim 9 wherein the hydrogen partial pressures is less than 10 psia.

11. The process according to claim 10 wherein the hydrogen partial pressure is less than 7 psia.

12. The process according to claim 1 wherein hydrogenation catalyst comprises a Group VIII metal or metal compound as the principal catalytic component.

13. The process according to claim 12 wherein said

catalyst comprises Pd.

14. The process according to claim 5 wherein said overhead pressure is in the range of 50 to 150 psia.

15. A process for the selective hydrogenation of highly unsaturated compounds comprising di-olefins and acetylenic compounds contained within a olefin rich stream, comprising the steps of:

(a) feeding (1) a first stream comprising olefins, di-olefins and acetylenic hydrocarbon compounds and (2) a second stream containing hydrogen to a distillation column reactor into a feed zone;

(b) concurrently in said distillation column reactor under a hydrogen partial pressure of about 0.1 psi to less than 50 psi:

(i) contacting said streams in a distillation reaction zone with a hydrogenation catalyst prepared in a form to act as a distillation structure thereby reacting essentially all of said di-olefins and acetylenic compounds with said hydrogen to form less unsaturated hydrocarbons in a reaction mixture, and

(ii) separating the olefins contained in said first stream and any olefins produced by said hydrogenation from said reaction mixture by fractional distillation.

16. The process according to claim 15 wherein said first stream is fed at or below the lower end of said distillation reaction zone.

17. The process according to claim 15 wherein said streams are fed separately to said distillation column reactor.

18. The process according to claim 15 wherein said first and second streams are mixed prior to entry into said distillation column reactor

19. The process according to claim 15 wherein said hydrocarbon stream comprises aliphatic compounds having three to nine carbon atoms.

20. The process according to claim 19 wherein said hydrocarbon stream comprises a C₃ fraction.

21. The process according to claim 19 wherein said

hydrocarbon stream comprises a C₄ cut.

22. The process according to claim 19 wherein said hydrocarbon stream comprises a C₅ cut.

23. The process according to claim 19 wherein said hydrocarbon stream comprises a C₆ cut.

24. The process according to claim 19 wherein said first and second streams are combined before feeding to said distillation column reactor.

25. The process according to claim 15 wherein hydrogenation catalyst comprises a Group VIII metal or metal compound as the principal catalytic component.

26. The process according to claim 25 wherein said hydrogenation catalyst comprises 0.1 to 5.0 wt% palladium oxide on alumina extrudates.

27. The process according to claim 15 wherein the overhead pressure of said distillation column reactor is between 240 and 315 psig.

28. The process according to claim 27 wherein said first stream comprises propylene.

29. The process according to claim 15 wherein said distillation structure comprises flexible, semi-rigid open mesh tubular material wire mesh, filed with a particulate hydrogenation catalytic material.

30. The process according to claim 15 further comprising step (c) withdrawing the separated olefins from step (b) (ii) along with any alkanes and lighter compounds, including any unreacted hydrogen, from said distillation column reactor as overheads.

31. The process according to claim 15 wherein said distillation column reactor operates at overhead pressure of in the range between 0 and 250 psig.

32. The process according to claim 31 wherein said pressure is in the range of 50 to 150 psig.

33. The process according to claim 15 wherein temperatures within said distillation reaction zone are in the range of 40 to 300°F.

34. The process according to claim 33 wherein temperatures within said distillation reaction zone are in

the range of 110 to 270°F.

35. The process according to claim 15 wherein substantially all of said di-olefins and acetylenic compounds are eliminated from said hydrocarbon stream.

36. The process according to claim 15 wherein the first stream has a WHSV in the range of 0.1 to 35.

37. The process according to claim 16 wherein hydrogenation catalyst comprises a Group VIII metal or metal compound as the principal catalytic component.

38. The process according to claim 37 wherein said hydrogenation catalyst comprises 0.1 to 5.0 wt% palladium oxide on alumina extrudates.

39. The process according to claim 37 wherein said distillation column reactor operates at overhead pressure of in the range between 0 and 250 psig.

40. The process according to claim 39 wherein temperatures within said distillation reaction zone are in the range of 40 to 300°F.

41. The process according to claim 40 wherein said pressure is in the range of 50 to 150 psig.

42. The process according to claim 41 wherein temperatures within said distillation reaction zone are in the range of 110 to 270°F.

43. The process according to claim 42 wherein the hydrogen partial pressure is in the range of 0.1 to 10 psia.

44. The process according to claim 43 wherein there is internal reflux in the range of 0.5 to 5 L/D.

45. The process according to claim 15 wherein substantially all of the highly unsaturated compounds are hydrogenated.

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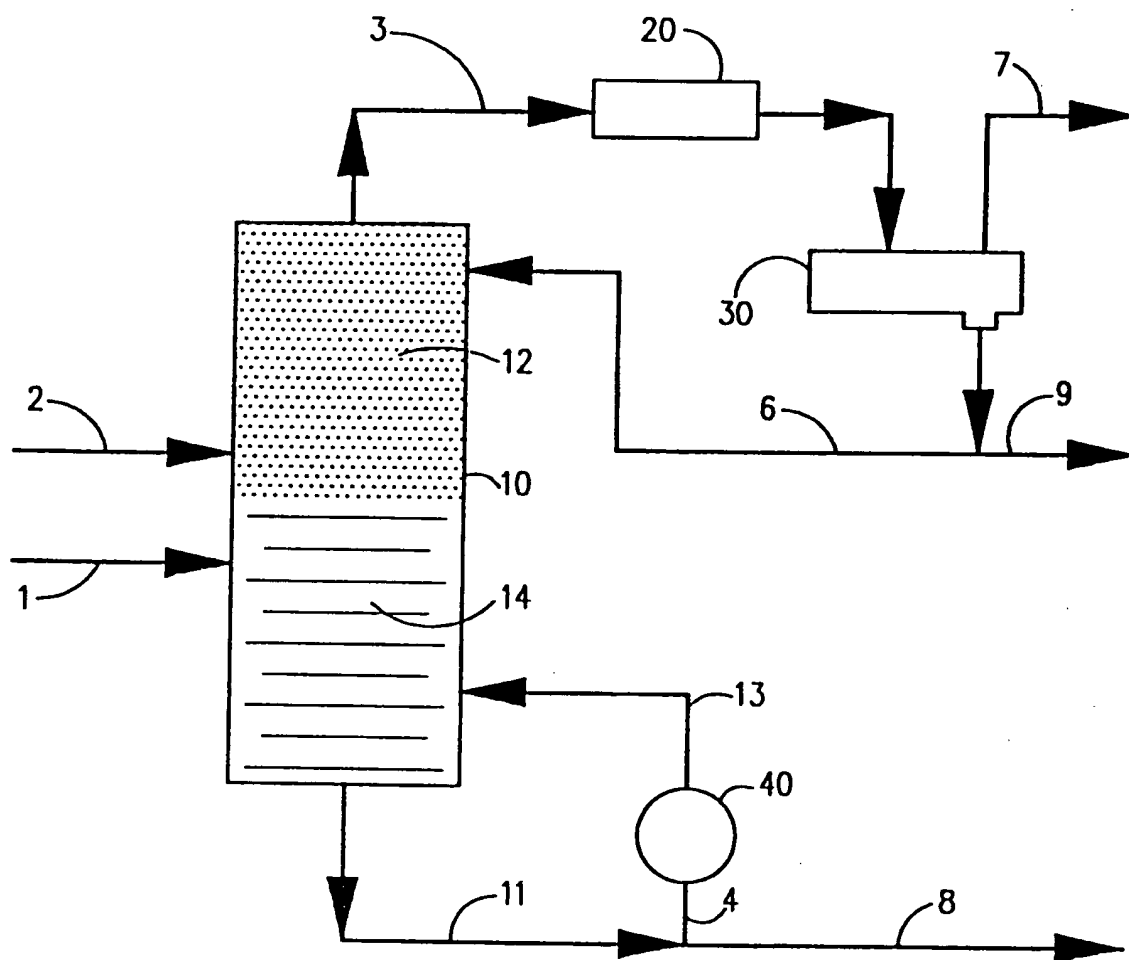


FIG. 1

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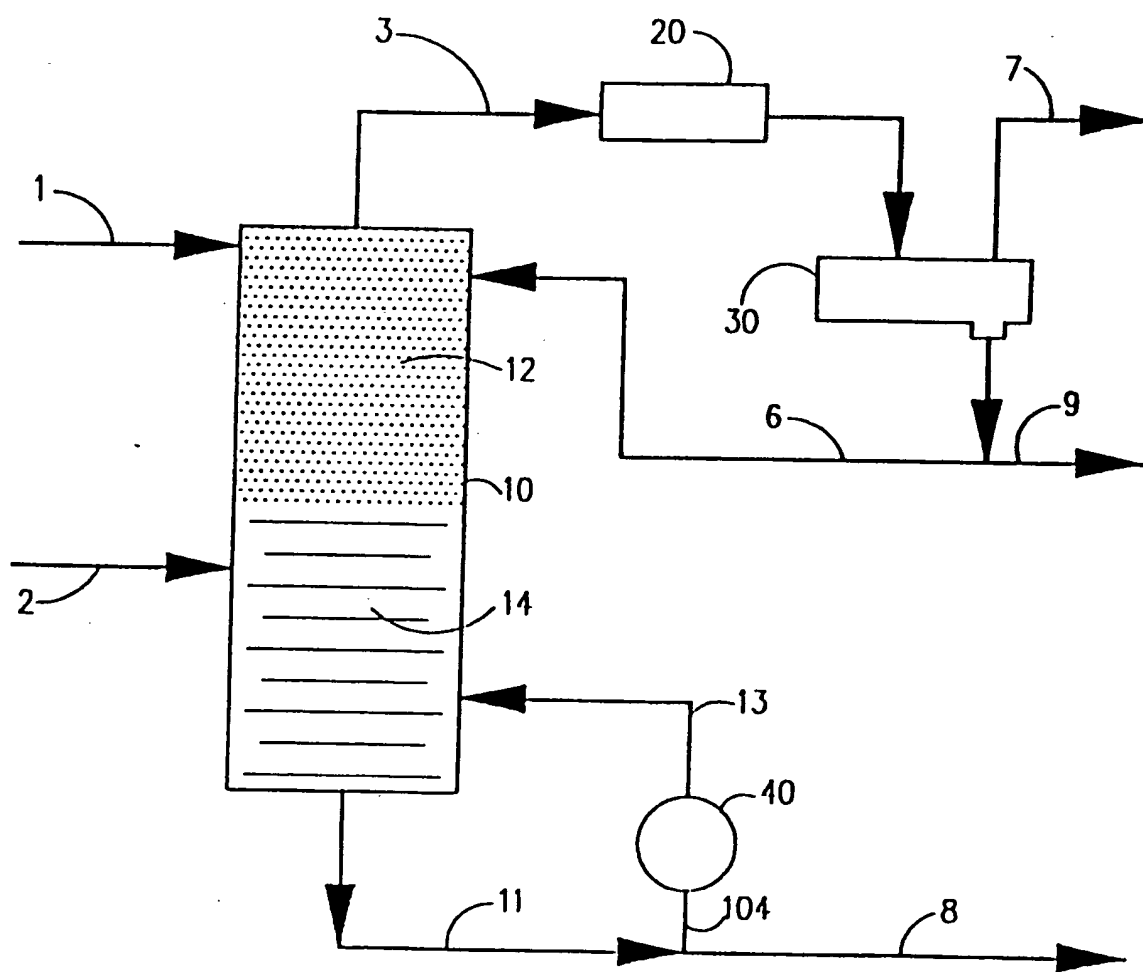


FIG. 2

3/4

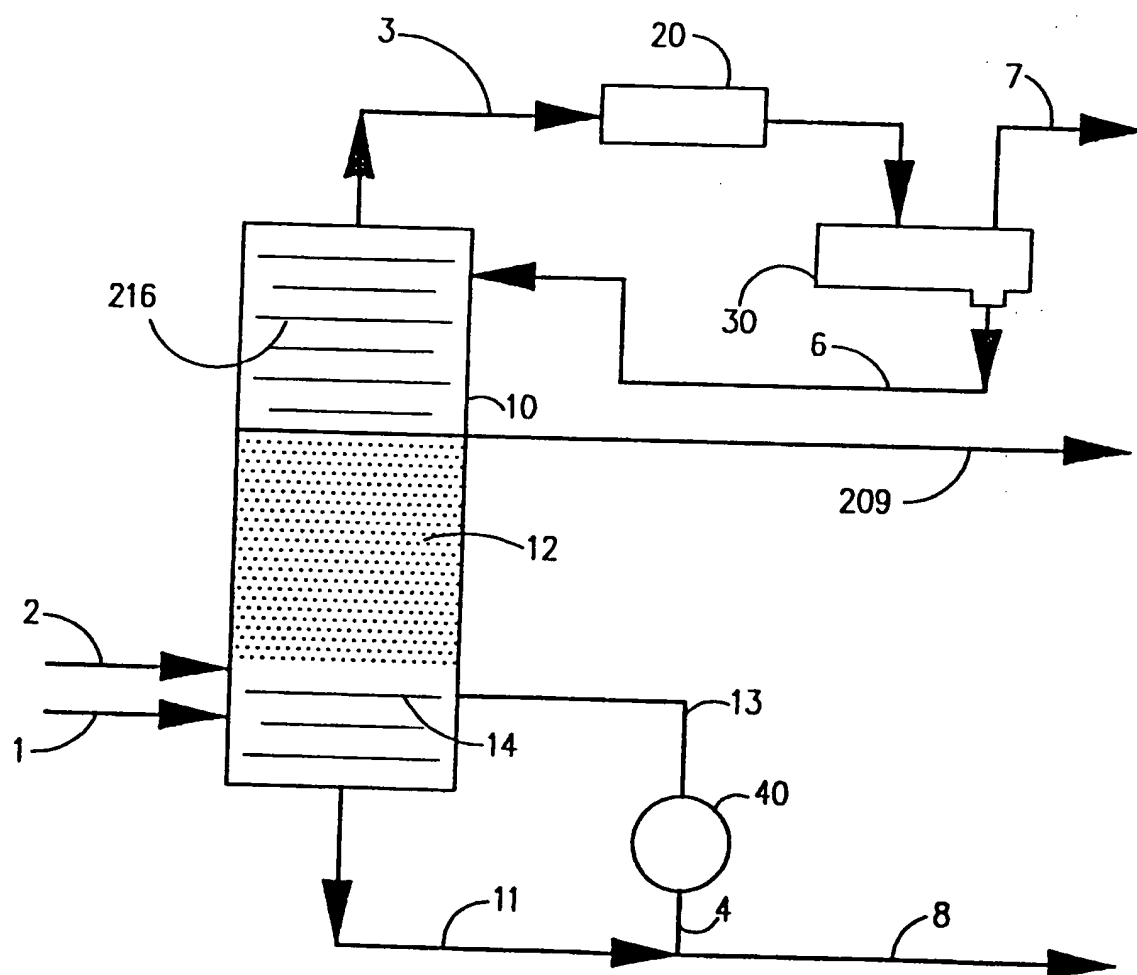


FIG. 3

4/4

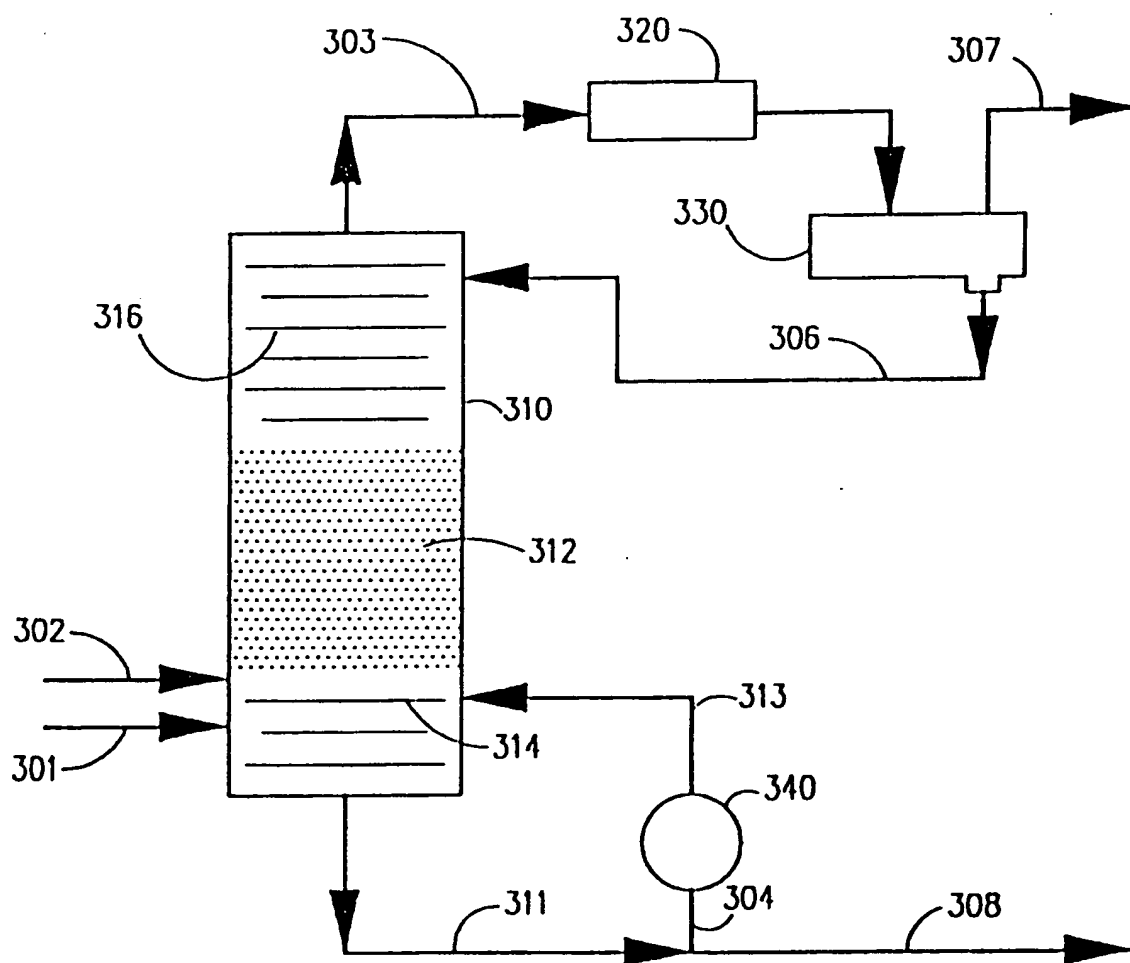


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07758

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C07C 5/05, 5/08, 5/09

US CL : 585/258, 259, 260, 261; 203/32, Digest 6

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/258, 259, 260, 261; 203/32, Digest 6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,215,011 (SMITH ET AL.), 29 JULY 1980, ALL PAGES	1-45
Y	US, A, 4,221,653 (CHERVENAK ET AL.) 09 SEPTEMBER 1980, ALL PAGES	1-45
A	US, A, 4,232,177 (SMITH ET AL.) 04 NOVEMBER 1980, ALL PAGES	1-45
Y	US, A, 4,439,350 (JONES, JR.) 27 MARCH 1984, ALL PAGES	1-45
Y	GB, A, 835,689 (BAYER) 25 MAY 1960, ALL PAGES	1-45

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

A	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*A*	document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

14 SEPTEMBER 1994

Date of mailing of the international search report

18 OCT 1994

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